



(19) Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number: 0 422 836 A2

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 90310889.2

(51) Int. Cl.<sup>5</sup>: G02B 1/04, C08G 18/75,  
C08G 18/38

(22) Date of filing: 04.10.90

(30) Priority: 09.10.89 JP 262204/89

Yokohama-shi, Kanagawa-ken(JP)

Inventor: Sasagawa, Katsuyoshi

1510 Shinyoshidacho, Kohoku-ku

Yokohama-shi, Kanagawa-ken(JP)

Inventor: Imai, Masao

1-11-10, Hashido, Seya-ku

Yokohama-shi, Kanagawa-ken(JP)

Inventor: Suzuki, Toshiyuki

4-1-28, Hase

Kamakura-shi, Kanagawa-ken(JP)

(43) Date of publication of application:  
17.04.91 Bulletin 91/16

(74) Representative: Stuart, Ian Alexander et al  
MEWBURN ELLIS 2 Cursitor Street  
London EC4A 1BQ(GB)

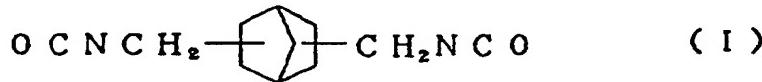
(64) Designated Contracting States:  
CH DE ES FR GB IT LI NL

(71) Applicant: MITSUI TOATSU CHEMICALS,  
INCORPORATED  
2-5, 3-chome, Kasumigaseki  
Chiyoda-ku Tokyo(JP)

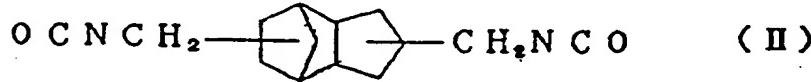
(72) Inventor: Kanemura, Yoshinobu  
2882, Iijimacho, Sakae-ku

(54) Resin for urethane lenses, lenses comprising the resin, and a process for preparation of the resin and the lenses.

(57) A resin for urethane lenses is here disclosed which is obtained by reacting an alicyclic isocyanate compound represented by the formula (I)



and/or an alicyclic isocyanate compound represented by the formula (II)



with at least one active hydrogen compound selected from polyol compounds, polythiol compounds except 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane, and thiol compounds having a hydroxyl group. In addition, lenses comprising this resin and processes for the preparation of the resin and the lenses are also disclosed herein.

EP 0 422 836 A2

**RESIN FOR URETHANE LENSES, LENSES COMPRISING THE RESIN, AND A PROCESS FOR PREPARATION OF THE RESIN AND THE LENSES**

The present invention relates to a resin for urethane lenses having good optical properties and heat resistance, to lenses comprising the resin, and to processes for the preparation of the resin and the lenses.

Plastic lenses are lighter and less breakable as compared with inorganic lenses, and are also dyeable. Therefore, in recent years, the application of plastic lenses to optical elements such as spectacles and cameras has increased rapidly.

A resin which presently has been widely used for this purpose can be obtained by the radical polymerization of diethylene glycol bis(allylcarbonate) (hereinafter referred to as "D.A.C"). This kind of resin is characterized by having excellent impact resistance, being lightweight, and having excellent dyeing properties, good workability such as cutting and polishing, and the like.

With regard to this resin, however, its refractive index is lower ( $n_D = 1.50$ ) than that of the inorganic lenses ( $n_D = 1.52$ ). Accordingly, in order to obtain the optical characteristics equal to those of glass lenses, it is necessary to increase the thickness of the center and periphery of the plastic lenses as well as their curvature, so that the thickness of the plastic lenses inevitably increases on the whole. For this reason, the resin for lenses having a higher refractive index is desired.

Furthermore, polyurethane resins are known as resins for lenses having a high refractive index which can be obtained by the reaction of an isocyanate compound and a hydroxy compound such as diethylene glycol (Japanese Patent Laid-open No. 57-136601), the reaction of the isocyanate compound and a hydroxy compound having a halogen atom such as tetrabromobisphenol A (Japanese Patent Laid-open No. 58-164615), and the reaction of the isocyanate compound and a hydroxy compound having a diphenyl sulfide skeleton (Japanese Patent Laid-open No. 60-194401).

Moreover, the same assignee as in this application has already offered, as resins for lenses having a high refractive index, polyurethane resins and lenses comprising the resins obtained by the reaction of an isocyanate compound and a hydroxy compound having a sulfur atom (Japanese Patent Laid-open No. 60-217229) and the reaction of the isocyanate compound and a polythiol compound (Japanese Patent Laid-open Nos. 60-199016, 62-267314 and 63-46213).

The lenses comprising these known resins have a higher refractive index than the lenses using D.A.C., but the degree of its improvement is not sufficient. Additionally, in these resins, compounds having many halogen atoms or an aromatic ring in each molecule thereof are used so as to improve the refractive index, and therefore they have some drawbacks, for example, poor weathering resistance and increased specific gravity.

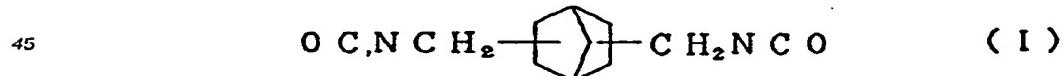
Moreover, in these known plastic lenses of the present applicants the refractive index is still poor; dispersion is more perceptible considering the value of the refractive index as compared with glass lenses; and heat resistance is insufficient in a subsequent step of dyeing, coating and the like. For these reasons, further improvement is demanded.

Thus it is desirable to provide a resin for urethane lenses having high refractive index, extremely low dispersion, excellent heat resistance and weathering resistance, being lightweight and having good impact resistance.

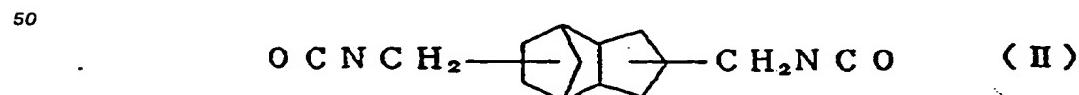
It is further desirable to provide lenses comprising the above-mentioned resin.

It is still further desirable to provide processes for preparing the above-mentioned resin and lenses.

In order to achieve the aforesaid objects, the present inventors have conducted further research concerning raw materials of a resin for urethane lenses, and as a result, have found that when an alicyclic isocyanate compound represented by the formula (I)



and/or an alicyclic isocyanate compound represented by the formula (II)



is reacted with at least one active hydrogen compound selected from polyol compounds, polythiol compounds except 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane, and thiol compounds having a hydroxyl group, a resin for urethane lenses can be obtained. A preferred embodiment has high refractive index, extremely low dispersion, excellent heat resistance and weathering resistance, and is lightweight and 5 has good impact resistance. The present invention has been achieved on the basis of this knowledge.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 Typical examples of the alicyclic isocyanate compound represented by the formula (I) used in the present invention include 2,5-bis(isocyanatomethyl)bicyclo[2.2.1]heptane and 2,6-bis(isocyanatomethyl)-bicyclo[2.2.1]heptane, and typical examples of the alicyclic isocyanate compound represented by the formula (II) include 3,8-bis(isocyanatomethyl)tricyclo[5.2.1.0<sup>2.6</sup>]-decane, 3,9-bis(isocyanatomethyl)tricyclo-[5.2.1.0<sup>2.6</sup>]-decane, 4,8-bis(isocyanatomethyl)tricyclo[5.2.1.0<sup>2.6</sup>]-decane and 4,9-bis(isocyanatomethyl)-tricyclo[5.2.1.0<sup>2.6</sup>]-decane. These compounds can be used singly or in the form of a mixture of two or more thereof.

Examples of a polyol compound used in the present invention are bifunctional or higher-functional polyols inclusive of compounds having a sulfur atom in each molecule thereof.

20 Typical examples of the bifunctional or higher-functional polyol compounds include polyols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, neopentyl glycol, glycerin, trimethylolethane, trimethylolpropane, butanetriol, 1,2-methyl glucoside, pentaerythritol, dipentaerythritol, tripentaerythritol, sorbitol, erythritol, slaytol, ribitol, arabinitol, xylitol, allitol, manitol, dulcitol, iditol, glycol, inositol, hexanetriol, triglycerol, diglycerol, triethylene glycol, polyethylene glycol, tris(2-hydroxyethyl)isocyanurate, cyclobutanediol, cyclopentanediol, cyclohexanediol, cycloheptanediol, cyclooctanediol, cyclohexanedimethanol, hydroxypropylcyclohexanol, tricyclo[5.2.1.0<sup>2.6</sup>]decanedimethanol, bicyclo-[4.3.0]nonanediol, dicyclohexanediol, tricyclo[5.3.1.1]dodecanediol, bicyclo[4.3.0]nonanediol, tricyclo-[5.3.1.1]dodecanediethanol, hydroxypropyltricyclo[5.3.1.1]dodecanol, spiro[3.4]octanediol, butylcyclohexanediol, 1,1-bicyclohexylidenediol, cyclohexanetriol, multitol, lactitol, dihydroxynaphthalene, trihydroxynaphthalene, tetrahydroxynaphthalene, dihydroxybenzene, benzenetriol, biphenyltetraol, pyrogallol, (hydroxynaphthyl)pyrogallol, trihydroxyphenanthrene, bisphenol A, bisphenol F, xylylene glycol, di(2-hydroxyethoxy)benzene, bisphenol A bis(2-hydroxyethyl) ether, tetrabromobisphenol A, tetrabromobisphenol A bis-(2-hydroxyethyl) ether, dibromoneopentyl glycol and epoxy resin; condensation reaction products of the above-mentioned polyols and organic polybasic acids such as oxalic acid, glutamic acid, adipic acid, acetic acid, propionic acid, cyclohexanecarboxylic acid, B-oxocyclohexanepropionic acid, dimeric acid, phthalic acid, isophthalic acid, salicylic acid, 3-bromopropionic acid, 2-bromoglycolic acid, dicarboxycyclohexane, pyromellitic acid, butanetetracarboxylic acid and phthalic acid; addition reaction products of the above-mentioned polyols and alkylene oxides such as ethylene oxide and propylene oxide; and addition reaction products of alkylene polyamines and alkylene oxides such as ethylene oxide and propylene oxide.

40 In addition, their halogen-substituted compounds such as chlorine-substituted compounds and bromine-substituted compounds can also be used.

They can be used singly or in the form of a mixture of two or more thereof.

Examples of the bifunctional or higher-functional polyols having a sulfur atom include bis[4-(2-hydroxyethoxy)phenyl] sulfide, bis[4-(2-hydroxypropoxy)phenyl] sulfide, bis[4-(2,3-dihydroxypropoxy)phenyl] sulfide, bis(4-hydroxycyclohexyl) sulfide, bis[2-methyl-4-(hydroxyethoxy)-6-butylphenyl] sulfide, compounds obtained by adding ethylene oxide and/or propylene oxide to the above-mentioned compounds usually in a ratio of three molecules of the former oxide to one hydroxyl group of each latter compound, di-(2-hydroxyethyl) sulfide, 1,2-bis(2-hydroxyethylmercapto)ethane, bis(2-hydroxyethyl) disulfide, 1,4-dithian-2,5-diol, bis(2,3-dihydroxypropyl) sulfide, tetrakis(4-hydroxy-2-thiabutyl)methane, bis(4-hydroxyphenyl)sulfone (trade name Bisphenol S), tetrabromobisphenol S, tetramethylbisphenol S, 4,4'-thiobis(6-tert-butylphenol) and 1,3-bis(2-hydroxyethylthioethyl)cyclohexane.

In addition, their halogen-substituted compounds such as chlorine-substituted compounds and bromine-substituted compounds can also be used.

They can be used singly or in the form of a mixture of two or more thereof.

55 Polythiol compounds used in the present invention are bifunctional and higher-functional, and these compounds also include compounds having at least one sulfur atom in addition to a mercapto group. However, 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane is omitted therefrom.

Typical examples of the bifunctional and more-functional polythiol include aliphatic polythiols such as

methanedithiol, 1,2-ethanedithiol, 1,1-propanedithiol, 1,2-propanedithiol, 1,3-propanedithiol, 2,2-propanedithiol, 1,6-hexanedithiol, 1,2,3-propanetri thiol, 1,1-cyclohexanedithiol, 1,2-cyclohexanedithiol, 2,2-dimethylpropane-1,3-dithiol, 3,4-dimethoxybutane-1,2-dithiol, 2-methylcyclohexane-2,3-dithiol, bicyclo[2.2.1]-hepta-exo-cis-2,3-dithiol, 1,1-bis(mercaptopropyl)cyclohexane, bis(2-mercaptoproethyl) thiomalate, (2-mercaptoproethyl) 2,3-dimercaptosuccinate, 2,3-dimercapto-1-propanol (2-mercaptoproacetate), 2,3-dimercapto-1-propanol (3-mercaptoproacetate), diethylene glycol bis(2-mercaptoproacetate), diethylene glycol bis(3-mercaptopropionate), 1,2-dimercaptotripropyl methyl ether, 2,3-dimercaptotripropyl methyl ether, 2,2-bis(mercaptopropyl)-1,3-propanedithiol, bis(2-mercaptoproethyl) ether, ethylene glycol bis(2-mercaptoproacetate), ethylene glycol bis(3-mercaptopropionate), trimethylolpropane tris(2-mercaptoproacetate), trimethylolpropane tris(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoproacetate) and pentaerythritol tetrakis(3-mercaptopropionate); their halogen-substituted compounds such as chlorine-substituted compounds and bromine-substituted compounds; aromatic polythiols such as 1,2-dimercaptobenzene, 1,3-dimercaptobenzene, 1,4-dimercaptobenzene, 1,2-bis(mercaptopropyl)benzene, 1,3-bis(mercaptopropyl)benzene, 1,4-bis(mercaptopropyl)benzene, 1,2-bis(mercaptoproethyl)benzene, 1,3-bis(mercaptoproethyl)benzene, 1,4-bis(mercaptoproethyl)benzene, 1,2-bis(mercaptoproxy)benzene, 1,3-bis(mercaptoproxy)benzene, 1,4-bis(mercaptoproxy)benzene, 1,2-bis(mercaptoproxybenzene), 1,3-bis(mercaptoproxybenzene), 1,4-bis(mercaptoproxybenzene), 1,2,3-trimercaptobenzene, 1,2,4-trimercaptobenzene, 1,3,5-trimercaptobenzene, 1,2,3-tris(mercaptopropyl)benzene, 1,2,4-tris(mercaptopropyl)benzene, 1,3,5-tris(mercaptopropyl)benzene, 1,2,3-tris(mercaptoproethyl)benzene, 1,2,4-tris(mercaptoproethyl)benzene, 1,3,5-tris(mercaptoproethyl)benzene, 1,2,3-tris(mercaptoproxy)benzene, 1,2,4-tris(mercaptoproxy)benzene, 1,3,5-tris(mercaptoproxy)benzene, 1,2,3-tris(mercaptoproxybenzene), 1,2,4-tris(mercaptoproxybenzene), 1,3,5-tris(mercaptoproxybenzene), 1,2,3,4-tetramercaptobenzene, 1,2,3,5-tetramercaptobenzene, 1,2,4,5-tetramercaptobenzene, 1,2,3,4-tetrakis(mercaptopropyl)benzene, 1,2,3,5-tetrakis(mercaptopropyl)benzene, 1,2,4,5-tetrakis(mercaptopropyl)benzene, 1,2,3,4-tetrakis(mercaptoproethyl)benzene, 1,2,3,5-tetrakis(mercaptoproethyl)benzene, 1,2,4,5-tetrakis(mercaptoproethyl)benzene, 1,2,3,4-tetrakis(mercaptoproxy)benzene, 1,2,3,5-tetrakis(mercaptoproxy)benzene, 1,2,4,5-tetrakis(mercaptoproxy)benzene, 1,2,3,4-tetrakis(mercaptoproxybenzene), 1,2,3,5-tetrakis(mercaptoproxybenzene), 1,2,4,5-tetrakis(mercaptoproxybenzene), 2,2-dimercaptobiphenyl, 4,4-dimercaptobiphenyl, 4,4-dimercaptobiphenyl, 2,5-toluenedithiol, 3,4-toluenedithiol, 1,4-naphthalenedithiol, 1,5-naphthalenedithiol, 2,6-naphthalenedithiol, 2,7-naphthalenedithiol, 2,4-dimethylbenzene-1,3-dithiol, 4,5-dimethylbenzene-1,3-dithiol, 9,10-anthracenedimethanethiol, 1,3-di(p-methoxyphenyl)-propane-2,2-dithiol, 1,3-diphenylpropane-2,2-dithiol, phenylmethane-1,1-dithiol and 2,4-di(p-mercaptophenyl)pentane; halogen-substituted aromatic polythiols such as chlorine-substituted compounds and bromine-substituted compounds, for example, 2,5-dichlorobenzene-1,3-dithiol, 1,3-di(p-chlorophenyl)-propane-2,2-dithiol, 3,4,5-tribromo-1,2-dimercaptobenzene and 2,3,4,6-tetrachloro-1,5-bis(mercaptopropyl)benzene; polythiols having a heterocyclic ring such as 2-methylamino-4,6-dithiol-sym-triazine, 2-ethylamino-4,6-dithiol-sym-triazine, 2-morpholino-4,6-dithiol-sym-triazine, 2-cyclohexylamino-4,6-dithiol-sym-triazine, 2-methoxy-4,6-dithiol-sym-triazine, 2-phenoxy-4,6-dithiol-sym-triazine, 2-thiobenzeneoxy-4,6-dithiol-sym-triazine and 2-thiobutyloxy-4,6-dithiol-sym-triazine; and their halogen-substituted compounds such as chlorine-substituted compounds and bromine-substituted compounds.

They can be used singly or in the form of a mixture of two or more thereof.

Examples of the bifunctional and more-functional polythiols having at least one sulfur atom in addition to the mercapto group include aromatic polythiols such as 1,2-bis(mercaptopropylthio)benzene, 1,3-bis(mercaptopropylthio)benzene, 1,4-bis(mercaptopropylthio)benzene, 1,2-bis(mercaptoethylthio)benzene, 1,3-bis(mercaptoethylthio)benzene, 1,4-bis(mercaptoethylthio)benzene, 1,2,3-tris(mercaptopropylthio)benzene, 1,2,4-tris(mercaptopropylthio)benzene, 1,3,5-tris(mercaptopropylthio)benzene, 1,2,3-tris(mercaptoethylthio)benzene, 1,2,4-tris(mercaptoethylthio)benzene, 1,3,5-tris(mercaptoethylthio)benzene, 1,2,3,4-tetrakis(mercaptopropylthio)benzene, 1,2,3,5-tetrakis(mercaptopropylthio)benzene, 1,2,4,5-tetrakis(mercaptopropylthio)benzene, 1,2,3,4-tetrakis(mercaptopropylthio)benzene, 1,2,3,5-tetrakis(mercaptopropylthio)benzene, 1,2,4,5-tetrakis(mercaptopropylthio)benzene and their nuclear-alkylated compounds; aliphatic polythiols such as bis(mercaptopropyl) sulfide, bis(mercaptoethyl) sulfide, bis(mercaptopropyl) sulfide, bis(mercaptopropylthio)methane, bis(2-mercaptoethylthio)methane, bis(3-mercaptopropylthio)methane, 1,2-bis(mercaptopropylthio)ethane, 1,2-bis(2-mercaptoethylthio)ethane, 1,2-bis(3-mercaptopropylthio)ethane, 1,3-bis(mercaptopropylthio)propane, 1,3-bis(2-mercaptoethylthio)propane, 1,3-bis(3-mercaptopropylthio)propane, 1,2,3-tris(mercaptopropylthio)propane, 1,2,3-tris(2-mercaptoethylthio)propane, 1,2,3-tris(3-mercaptopropylthio)propane, tetrakis(mercaptopropylthiomethyl)methane, tetrakis(2-mercaptoethylthiomethyl)methane, tetrakis(3-mercaptopropylmethyl)methane, bis(2,3-dimercaptopropyl) sulfide, 2,5-dimercapo-1,4-dithian, bis(mercaptopropyl) disulfide, bis(mercaptoethyl) disulfide, bis(mercaptopropyl) di-

sulfide and their esters of thioglycollic acid and mercaptopropionic acid, hydroxymethylsulfido bis(2-mercaptopacetate), hydroxymethylsulfido bis(3-mercaptopropionate), hydroxyethylsulfido bis(2-mercaptopacetate), hydroxyethylsulfido bis(3-mercaptopropionate), hydroxypropylsulfido bis(2-mercaptopacetate), hydroxypropylsulfido bis(3-mercaptopropionate), hydroxymethyldisulfido bis(2-mercaptopacetate), hydroxymethyldisulfido bis(3-mercaptopropionate), hydroxyethyldisulfido bis(2-mercaptopacetate), hydroxyethyldisulfido bis(3-mercaptopropionate), hydroxypropyldisulfido bis(2-mercaptopacetate), hydroxypropyldisulfido bis(3-mercaptopropionate), 2-mercptoethyl ether bis(2-mercaptopacetate), 2-mercptoethyl ether bis(3-mercaptopropionate), 1,4-dithian-2,5-diol bis(2-mercaptopacetate), 1,4-dithian-2,5-diol bis(3-mercaptopropionate), bis(2-mercptoethyl) thiodiglycolate, bis(2-mercptoethyl) thiodipropionate, bis(2-mercptoethyl) 4,4-thiodibutylate, bis(2-mercptoethyl) dithiodiglycolate, bis(2-mercptoethyl) dithiodipropionate, bis(2-mercptoethyl) 4,4-dithiodibutylate, bis(2,3-dimercaptopropyl) thiodiglycolate, bis(2,3-dimercaptopropyl) thiodipropionate, bis(2,3-dimercaptopropyl) dithiodiglycolate, bis(2,3-dimercaptopropyl) dithiodipropionate; and compounds having a heterocyclic ring such as 3,4-thiophenedithiol and bismuthiol.

Additionally, their halogen-substituted compounds such as chlorine-substituted compounds and bromine-substituted compounds can also be used:

They can be used singly or in the form of a mixture of two or more thereof.

Examples of a thiol compound having a hydroxyl group used in the present invention include compounds having at least one sulfur atom in addition to a mercapto group.

Typical examples of such compounds include 2-mercptoethanol, 3-mercpto-1,2-propanediol, glycerin di(mercaptopacetate), 1-hydroxy-4-mercaptocyclohexane, 2,4-dimercaptophenol, 2-mercaptophydroquinone, 4-mercaptophenol, 3,4-dimercapo-2-propanol, 1,3-dimercapo-2-propanol, 2,3-dimercapo-1-propanol, 1,2-dimercapo-1,3-butanediol, trimethylolpropane bis(thioglycolate), trimethylolpropane bis(3-mercaptopropionate), trimethylolpropane mono(thioglycolate), trimethylolpropane mono(3-mercaptopropionate), pentaerythritol tris(3-mercaptopropionate), pentaerythritol mono(3-mercaptopropionate), pentaerythritol bis(3-mercaptopropionate), pentaerythritol tris(thioglycolate), dipentaerythritol pentakis(3-mercaptopropionate), hydroxymethyltris(mercptoethylthiomethyl)methane, 1-hydroxyethylthio-3-mercptoethylthiobenzene, 4-hydroxy-4-mercaptopdiphenylsulfone, 2-(2-mercptoethylthio)ethanol, dihydroxyethylsulfido mono(3-mercaptopropionate), dimercptoethane mono(salicylate), hydroxyethylthiomethyl-tris(mercptoethylthiomethyl)-methane.

Additionally, their halogen-substituted compounds such as chlorine-substituted compounds and bromine-substituted compounds can also be used.

They can be used singly or in the form of a mixture of two or more thereof.

A ratio of the alicyclic isocyanate compound represented by the formula (I) and/or the formula (II) to the active hydrogen compound is such that the molar ratio of functional groups represented by NCO/(SH + OH) is usually in the range of from 0.5 to 3.0, preferably from 0.5 to 1.5.

The resins of the present invention are the urethane resin and/or the S-alkyl thiocarbamate resin, and their main chemical linkages are the urethane bond of an isocyanate group and a hydroxyl group and/or a mercapto group, and/or an S-alkyl thiocarbamate bond, but needless to say, other bonds can be additionally contained therein such as an allophanate bond, a urea bond and a biuret bond, depending upon the intended purpose. For example, the urethane bond or the S-alkyl thiocarbamate bond can be further reacted with the isocyanate group so as to increase the crosslink density, which often leads to preferable results. In this case, a reaction temperature is raised up to at least 100 °C and the isocyanate component is used in large quantities. Alternatively, an amine or the like can be partially used in order to utilize the urea bond or the biuret bond.

In case there are used such compounds other than the polyol compounds, the polythiol compounds except 1,2-bis[(2-mercptoethyl)thio]-3-mercaptopropane and the thiol compounds having a hydroxyl group which react with the isocyanate compound, much attention should be paid to the point of coloring.

Furthermore, as in a known molding process, a variety of additives may be added to the raw materials, if necessary, which are, for example, a chain extender, a crosslinking agent, a light stabilizer, an ultraviolet absorber, an antioxidant, an oil-soluble dye, a filler and so on.

For the purpose of adjusting a reaction rate to a desired level, it is also possible to add a suitable amount of a known reaction catalyst which is usable in the manufacture of S-alkyl thiocarbamate or polyurethane.

The lenses of the present invention can be obtained by cast polymerization.

Concretely, the alicyclic isocyanate compound represented by the formula (I) and/or the alicyclic isocyanate compound represented by the formula (II) is mixed with at least one active hydrogen compound selected from the group consisting of the polyol compounds, the polythiol compounds except 1,2-bis[(2-mercptoethyl)thio]-3-mercaptopropane, and the thiol compounds having a hydroxyl group. The resulting

mixture is then defoamed in a suitable manner, if necessary, and it is poured into a mold. Afterward, polymerization is usually carried out by gradually heating the mixture from a low temperature to a high temperature.

The resin for urethane lenses of the present invention which can be obtained in this way has high refractive index, extremely low dispersion, excellent heat resistance and weathering resistance, is lightweight and has good impact resistance, and therefore it is desirable as a material for optical lenses of spectacles, cameras and the like.

The lenses prepared from the resin material of the present invention can be subjected to a physical or a chemical treatment such as a surface polishing treatment, an antistatic treatment, a hard coat treatment, a non-reflecting treatment, a dyeing treatment or a dimming treatment so as to improve reflection inhibition, abrasion resistance and chemical resistance and to provide high hardness and cloud prevention.

Now, the present invention will be described in more detail in reference to examples and reference examples. For the obtained resins for lenses, performance tests of refractive index, Abbe's number, weathering resistance, heat resistance and appearance were carried out by the following methods.

Refractive index and Abbe's number: Each measurement was made at 20 °C by the use of a Pulfrich refractometer.

Weathering resistance: Each resin for a lens was set on a Weather-O-meter equipped with a sunshine carbon arc lamp, and after 200 hours had passed, the lens was taken out. Afterward, the hue of the lens was compared with that of the resin for the lens prior to the test. Evaluation was made by classifying the change of the hue into no change (O), slight yellowing ( $\Delta$ ) and yellowing (X).

Heat resistance: A heat deformation starting temperature was measured by loading each test piece with a weight of 5 g and then heating the same at 2.5 °C/minute by the use of a thermomechanical analyzer (manufactured by Perkin Elmer Co., Ltd. in U.S.A.).

Appearance: Observation was visually made.

25

#### Example 1

40 g of a mixture of 2,5-bis(isocyanatomethyl)bicyclo[2.2.1]heptane and 2,6-bis(isocyanatomethyl)-bicyclo[2.2.1]heptane (1:1) was mixed with 42.8 g of tetrakis(2-mercaptoproethylthiomethyl)methane, and 0.08 g of dibutyltin dilaurate was then added thereto, followed by forming a uniform mixture. Afterward, the mixture was poured into a mold comprising a glass mold and a gasket, and then heated to cure. The thus obtained resin was colorless and transparent and excellent in weathering resistance, and had a refractive index  $n_D$  of 1.62, an Abbe's number  $\nu_D$  of 42 and a heat deformation starting temperature of 120 °C.

35

#### Example 2

47.8 g of a mixture of 3,8-bis(isocyanatomethyl)tricyclo[5.2.1.0<sup>2,6</sup>]decane, 3,9-bis(isocyanatomethyl)-tricyclo[5.2.1.0<sup>2,6</sup>]decane, 4,8-bis(isocyanatomethyl)tricyclo[5.2.1.0<sup>2,6</sup>]decane and 4,9-bis(isocyanatomethyl)-tri cyclo[5.2.1.0<sup>2,6</sup>]decane was mixed with 42.8 g of tetrakis(2-mercaptoproethylthiomethyl)methane, and 0.09 g of dibutyltin dilaurate was then added thereto, followed by forming a uniform mixture. Afterward, the mixture was poured into a mold comprising a glass mold and a gasket, and then heated to cure. The thus obtained resin was colorless and transparent and excellent in weathering resistance, and had a refractive index  $n_D$  of 1.62, an Abbe's number  $\nu_D$  of 41 and a heat deformation starting temperature of 125 °C.

#### Examples 3 to 8, Comparative Examples 1 to 2

50 The same procedure as in Examples 1 and 2 was effected in order to synthesize resins having compositions shown in Table 1. The results of evaluation are set forth in Table 1.

Table 1 (I)

Isocyanate Compound (mole of isocyanato group)		Active Hydrogen Compound (mole of active hydrogen group)
Example 3	Isocyanate having the same composition as in Example 1 (1.0)	Pentaerythritol tetrakis(3-mercaptopropionate) (1.0)
Example 4	Isocyanate having the same composition as in Example 2, (1.0)	Pentaerythritol tetrakis(3-mercaptopropionate) (1.0)
Example 5	Isocyanate having the same composition as in Example 1 (1.0)	Tetrakis(2-hydroxyethylthiomethyl)methane (1.0)
Example 6	Isocyanate having the same composition as in Example 2 (1.0)	Tetrakis(2-hydroxyethylthiomethyl)methane (1.0)
Example 7	Isocyanate having the same composition as in Example 1 (1.0)	Glycerin 1,3-bis(2-mercaptopoacetate) (1.0)
Example 8	Isocyanate having the same composition as in Example 2 (1.0)	Glycerin 1,3-bis(2-mercaptopoacetate) (1.0)

5

10

15

20

25

30

35

40

45

50

55

Table 1 (II)

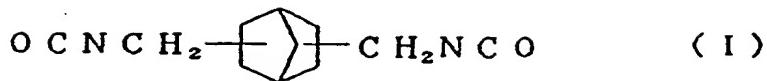
	Isocyanate Compound (mole of isocyanato group)	Active Hydrogen Compound (mole of active hydrogen group)
Comparative Example 1	Hexamethylene diisocyanate (1.0)	Pentaerythritol tetrakis(3- mercaptopropionate) (1.0)
Comparative Example 2	Xylylene diisocyanate (1.0)	Pentaerythritol tetrakis(3- mercaptopropionate) (1.0)

Table 1 (III)

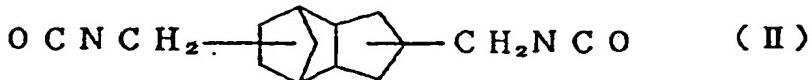
	$n_D$	$\nu_D$	Weathering Resistance	Heat Resistance (°C)	Colorless & transparent Appearance
Example 3	1.56	51	0	118	Colorless & transparent
Example 4	1.56	50	0	122	Colorless & transparent
Example 5	1.56	45	0	145	Colorless & transparent
Example 6	1.56	45	0	143	Colorless & transparent
Example 7	1.55	45	0	102	Colorless & transparent
Example 8	1.55	46	0	105	Colorless & transparent
Comparative Example 1	1.56	44	0	61	Colorless & transparent
Comparative Example 2	1.59	36	0	84	Colorless & transparent

## Claims

- 55 1. A resin for urethane lenses which is obtained by reacting an alicyclic isocyanate compound represented by the formula (I)



5 and/or an alicyclic isocyanate compound represented by the formula (II)



10

with at least one active hydrogen compound selected from polyol compounds, polythiol compounds except 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane, and thiol compounds having a hydroxyl group.

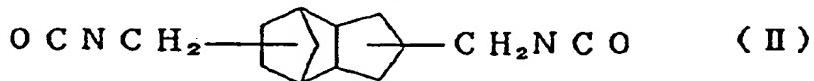
15 2. A resin for urethane lenses according to Claim 1 wherein the ratio of the alicyclic isocyanate compound to the active hydrogen compound is such that the molar ratio of functional groups represented by NCO/(SH + OH) is in the range of from 0.5 to 3.0.

3. A lens comprising a urethane resin which is obtained by reacting an alicyclic isocyanate compound represented by the formula (I)

20



25 and/or an alicyclic isocyanate compound represented by the formula (II)



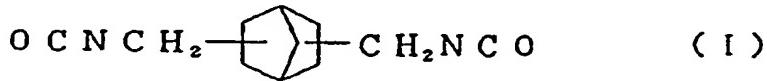
30

with at least one active hydrogen compound selected from polyol compounds, polythiol compounds except 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane, and thiol compounds having a hydroxyl group.

35 4. A lens according to Claim 3 wherein the ratio of the alicyclic isocyanate compound to the active hydrogen compound is such that the molar ratio of functional groups represented by NCO/(SH + OH) is in the range of from 0.5 to 3.0.

5. A process for preparing a resin for urethane lenses which comprises the steps of mixing an alicyclic isocyanate compound represented by the formula (I)

40



45

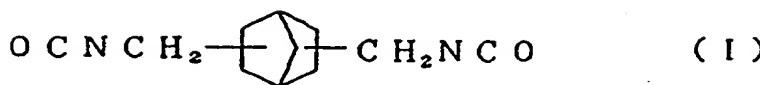
and/or an alicyclic isocyanate compound represented by the formula (II)



50 5. with at least one active hydrogen compound selected from polyol compounds, polythiol compounds except 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane, and thiol compounds having a hydroxyl group, and then heating and curing the mixture.

55 6. A process for preparing a resin for urethane lenses according to Claim 5 wherein the ratio of the alicyclic isocyanate compound to the active hydrogen compound is such that the molar ratio of functional groups represented by NCO/(SH + OH) is in the range of from 0.5 to 3.0.

7. A process for preparing lenses which comprises the steps of mixing an alicyclic isocyanate compound represented by the formula (I)



5 and/or an alicyclic isocyanate compound represented by the formula (II)



10

with at least one active hydrogen compound selected from polyol compounds, polythiol compounds except 1,2-bis[(2-mercaptopethyl)thio]-3-mercaptopropane, and thiol compounds having a hydroxyl group, and the cast-polymerizing the mixture.

15 8. A process for preparing lenses according to Claim 7 wherein the ratio of the alicyclic isocyanate compound to the active hydrogen compound is such that the molar ratio of functional groups represented by NCO/(SH + OH) is in the range of from 0.5 to 3.0.

20

25

30

35

40

45

50

55





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

0 422 836 A3

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 90310889.2

(51) Int. Cl.5: G02B 1/04, C08G 18/75,  
C08G 18/38

(22) Date of filing: 04.10.90

(30) Priority: 09.10.89 JP 262204/89

(72) Inventor: Kanemura, Yoshinobu  
2882, Iijimacho, Sakae-ku  
Yokohama-shi, Kanagawa-ken(JP)  
Inventor: Sasagawa, Katsuyoshi  
1510 Shinyoshidacho, Kohoku-ku  
Yokohama-shi, Kanagawa-ken(JP)  
Inventor: Imai, Masao  
1-11-10, Hashido, Seya-ku  
Yokohama-shi, Kanagawa-ken(JP)  
Inventor: Suzuki, Toshiyuki  
4-1-28, Hase  
Kamakura-shi, Kanagawa-ken(JP)

(43) Date of publication of application:  
17.04.91 Bulletin 91/16

(74) Representative: Stuart, Ian Alexander et al  
MEWBURN ELLIS 2 Cursitor Street  
London EC4A 1BQ(GB)

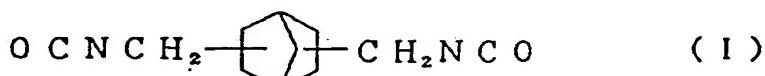
(84) Designated Contracting States:  
CH DE ES FR GB IT LI NL

(88) Date of deferred publication of the search report:  
03.07.91 Bulletin 91/27

(71) Applicant: MITSUI TOATSU CHEMICALS,  
INCORPORATED  
2-5, 3-chome, Kasumigaseki  
Chiyoda-ku Tokyo(JP)

(54) Resin for urethane lenses, lenses comprising the resin, and a process for preparation of the resin and the lenses.

(57) A resin for urethane lenses is here disclosed which is obtained by reacting an alicyclic isocyanate compound represented by the formula (I)



and/or an alicyclic isocyanate compound represented by the formula (II)



with at least one active hydrogen compound selected from polyol compounds, polythiol compounds except 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane, and thiol compounds having a hydroxyl group. In addition, lenses comprising this resin and processes for the preparation of the resin and the lenses are also disclosed herein.

EP 0 422 836 A3



European  
Patent Office

EUROPEAN SEARCH  
REPORT

Application Number

EP 90 31 0889

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 329 386 (MITSUI TOATSU CHEMICALS) * Claims 1,2,9,10; page 3, lines 30-40 * -----	1	G 02 B 1/04 C 08 G 18/75 C 08 G 18/38
Y	US-A-4 689 387 (MITSUI TOATSU CHEMICALS) * Claim 1 * -----	1	
Y	DE-A-3 010 626 (HÜLS) * Claim 1; page 2, lines 1-9 * -----	1	
A	EP-A-0 329 389 (MITSUI TOATSU) * Claim 1 * -----	1	
A	EP-A-0 329 388 (MITSUI TOATSU) * Claims 1,10 * -----	1	

TECHNICAL FIELDS  
SEARCHED (Int. Cl.5)

G 02 B  
C 08  
G  
B 29 D

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	03 April 91	DEPIJPER R.D.C.
CATEGORY OF CITED DOCUMENTS		
X: particularly relevant if taken alone		E: earlier patent document, but published on, or after the filing date
Y: particularly relevant if combined with another document of the same category		D: document cited in the application
A: technological background		L: document cited for other reasons
O: non-written disclosure		&: member of the same patent family, corresponding document
P: intermediate document		
T: theory or principle underlying the invention		